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DETERMINATION OF DIOXINS IN DYES AND PIGMENTS WITH HRGC/HRMS[1]

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Dioxins in some textile dyes and pigments may be a significant source of both human exposure and environmental contamination. Dyes and pigments contaminated with dioxins are the main sources of dioxins in textile industry. Further formations of dioxins can occur via dyeing and textile finishing processes at the conditions favoured for the generation of PCDD/Fs (high temperatures, alkaline conditions, UV radiation or other radical starters). Distribution of dioxins and their fate during textile processes were investigated. Textile disperse dye contaminated with dioxins was used in dyeing process and increasing of dioxins content during the process was observed.

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Introduction

Textile products often contain chemicals such as formaldehyde, azo-dyes, dioxins and pesticides as well as heavy metals which might pose a risk to humans and the environment. Some of those found in finished products are residues from production, others are added to give certain characteristics to the products (colour, flame retardancy, etc.).

Dioxins

Dioxin is a term for a group of poly-halogenated aromatic hydrocarbons including 75 polychlorinated dibenzo-*p*-dioxins (PCDDs) and 135 polychlorinated dibenzofurans (PCDFs) [1]. Dioxins are persistent, toxic pollutants that accumulate in animal fat. Exposure to even low doses of dioxins can lead to cancer, damage of the nervous system, immune system diseases and reproductive disorders. Their structure is very similar, differing only in the number and spatial arrangement of chlorine atoms in the molecule. Isomers with chlorine atoms at position 2,3,7,8 are especially toxic (Fig. 1). The so-called "dirty group" includes 17 isomers of PCDD/Fs. Thermal processes are the main source of dioxins. They are formed in the gas phase at temperatures above 600 °C and on the surface of solid phase in the temperature range between 225 °C and 400 °C [2]. Chemical industry is an important source of dioxins (PCDD/PCDFs) as by-products [3]. PCDD/PCDFs can be formed during the synthesis of chlorophenols, chlorobenzenes, chlorobiphenyls, polyvinyl chloride, dyes, pigments, printing inks and halogenated pesticides. Known sources of PCDD/Fs are dioxazine dyes and pigments, produced from chloranil. Chloranil is produced from chlorinated phenols and during the synthesis PCDD/Fs are formed as by-products.

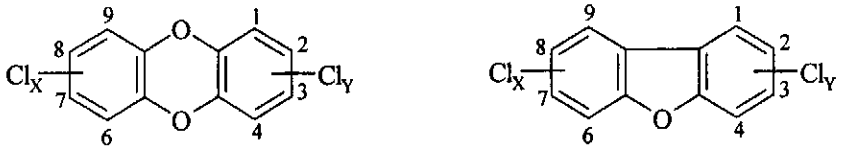

Fig. 1 Molecular structure of the polychlorinated dibenzo-*p*-dioxins (a) and polychlorinated dibenzofurans (b)

Dioxins in Textile Industry

The textile industry is being targeted as a potential source of PCDD/Fs as [4]:

- Pesticides such as pentachlorophenol, known to be contaminated with PCDD/Fs. Pentachlorophenol is used as a biocide for cotton and other materials
- Dyestuffs contaminated with PCDD/Fs
- Textile processes may utilize chlorinated chemicals contaminated with PCDD/Fs
- Washing processes in alkaline media are part of the textile finishing processes,
- Formation of PCDD/Fs may occur upon incineration of textiles

PCDD/Fs were detected in sewage sludges tested in Germany [5]. On the basis of a study of the potential sources of PCCD/Fs in sewage sludge, it was concluded that the contribution of several textile products could account for the presence of PCDD/Fs in many municipal wastewater treatment plants [6]. Therefore, a logical category of products were tested to determine the sources of dioxins.

The concentrations of PCDD/Fs determined in various new garments ranging from low pg g^{-1} to high 300 ng g^{-1}, with the OCDD as the dominant homologue [7]. Dioxin homologue patterns that were found in more contaminated textile samples were annotated to PCDD/F patterns connected with pentachlorophenol and chloranil based dyes.

Contamination of the textile fibres during production and finishing was also investigated [8]. Cotton cloth was subjected to series of 16 typical finishing processes and analysed for PCDD/Fs at various stages of treatment. The maximum concentrations found in the raw textile products were 30 ng kg^{-1} in cotton and 45 ng kg^{-1} in synthetic materials. The concentration increase during treatment processes was attributable to an increase in OCDD. The contribution of textile production and finishing to the PCDD/Fs concentration increase with dyeing and with wash and wear finishing processes resulted in the maximum concentration of 100 ng kg^{-1}. In this study only a few textile processes were investigated covering a small range of chemicals used in the textile industry. In addition, the concentrations in wastewaters and used chemicals were not determined.

Dioxins in Dyes and Pigments

Synthesis of colorants represents a relatively large group of chemicals with complex synthesis processes. During synthesis of some colorants polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) can be formed. Dioxins are related to halogens, especially chlorine and bromine derivatives are

most toxic and persistent. About 40 % of worldwide used colorants contain organically bounded chlorine. Further formations of PCDD/Fs can occur *via* dyeing and textile finishing processes at conditions favoured for the generation of PCDD/Fs (high temperatures, alkaline conditions, UV radiation or other radical starters).

A relatively small number of data is available for PCDD/Fs content in textile dyes and pigments. Considerable levels of PCDD/Fs were determined in some dioxazine dyes and pigments, phtalocyanine dyes and in printing inks. Concentrations found in Direct Blue 106 dye, Direct Blue 108 dye and Violet 23 pigment were in the $\mu g\,kg^{-1}$ range with OCDD and OCDF as the dominant homologues [9]. Dioxazine pigments were derived from chloranil, which was found to contain high levels of PCDD/Fs and has been suggested as the source of contamination. In a sample of Ni-phthalocyanine dye, higher congeners of PCDD/Fs were found in $\mu g\,kg^{-1}$ concentration level. No PCDD/Fs were detected in two samples of Cu-phthalocyanine dyes and in one Co-phthalocyanine dye. Considerable levels of PCDD/Fs were determined also in some printing inks obtained from a supplier in Germany [10]. The identities of the dyes and pigments in these inks were not reported.

Methods and Materials

Determination of Dioxins

Analytical procedure for the determination of PCDD/Fs is quite complicated because concentrations of dioxins are low, comparing to the other chlorinated aromatic compounds like polychlorinated biphenyl ethers and polychlorinated biphenyls present in samples. High efficiency of the cleanup methods is necessary to make the analysis possible. Organic solvent extraction and cleanup of the extract by multi-step column chromatography is used. The quantification of dioxins is based on isotope dilution procedure with use of isotopically labelled ^{13}C-PCDD/Fs. The final determination of PCDD/Fs in the sample extract is carried out using high resolution gas chromatographic separation and high resolution mass spectrometric determination (HRGC/HRMS) with selected ion monitoring at resolution of 10,000.

Determination of PCDD/Fs in Dye Samples

Dye samples were spiked with an internal standard mixture containing $^{13}C_{12}$-labeled isomers, diluted in ethanol-water mixture and extracted with hexane. Cleanup of the extract was performed on a mixed column (layers: silica

gel/sulphuric acid, silica gel/KOH and silica gel) followed by the additional cleaning using adsorption chromatography on graphitised carbon column. Quantification was performed using high resolution gas chromatography/high resolution mass spectrometry (Finnigan MAT 95PL) at resolution of 10,000.

Dyeing Process

A disperse dye which contains PCDD/Fs was used in an industrial polypren fibres dyeing process. Two dyeing experiments were separately performed with 9 g of polypren fibres. Dyeing was carried out in a laboratory scale dyeing machine equipped with infrared heating, in stainless steel dyepots of 200 cm^3 capacity. The dye-bath was maintained at 130 °C for 45 min. After dyeing, the sample reduction clearing was carried out by heating in an aqueous solution containing sodium dithionite ($Na_2S_2O_4$) and sodium hydroxide at 70 °C. After the treatment, the samples were rinsed with distilled water and dried in air. Concentration of PCDD/Fs was determined in the coloured polypren and in the dye-bath.

Results

All determinations were made in duplicate and the results given are the mean values of the two measurements. Prior the dyeing experiments, all the laboratory glassware were rinsed with toluene-acetone mixture. Concentrations of PCDD/Fs were determined in raw polypren fabrics and in reagents. The concentrations of PCDD/Fs in these samples were close to the detection limit.

Six samples of disperse dyes were analysed for PCDD/Fs content (Table I).

Table I Concentrations of PCDD/Fs in disperse dyes

	Concentration, pg g^{-1}					
Congener/Group	Dye 1	Dye 2	Dye 3	Dye 4	Dye 5	Dye 6
Σ TCDD (tetra dioxins)	ND (< 5)	ND (< 5)	ND (< 5)	ND (< 5)	ND (< 5)	ND (< 5)
Σ PCDD (penta dioxins)	10	24	ND (< 5)	ND (< 5)	ND (< 5)	ND (< 5)
Σ H6CDD (hexa dioxins)	824	2405	ND (< 5)	ND (< 5)	27	ND (< 5)
Σ H7CDD (hepta dioxins)	1954	6396	128	ND (< 5)	ND (< 5)	ND (< 5)
OCDD (octa dioxin)	5928	15826	331	26	38	9
Σ TCDF (tetra furans)	700	301	38	ND (< 5)	ND (< 5)	ND (< 5)
Σ PCDF (penta furans)	426	954	12	ND (< 5)	6	ND (< 5)
Σ H6CDF (hexa furans)	759	1096	15	ND (< 5)	98	ND (< 5)
Σ H7CDF (hepta furans)	181	1014	ND (< 5)	ND (< 5)	26	ND (< 5)
OCDF (octa furan)	80	127	ND (< 5)	27	25	ND (< 5)
Sum PCDD/F	14350	28143	524	53	220	9
Sum 2,3,7,8 PCDD/Fs	7638	22279	406	53	182	9

In two disperse black dyes, a mixture of anthraquinone and azo-disperse dye, considerable level of PCDD/Fs was determined. The OCDD was the dominant compound. Distribution of dioxins and their fate during textile processes were further investigated. After textile finishing processes with contaminated disperse dye the content of the PCDD/Fs was approximately tenfold higher. There is strong evidence that PCDD/Fs are formed from precursor compounds present in contaminated dyes during textile finishing processes.

TableII Mass balance of PCDD/Fs for dyeing process

Congener/Group	Input-0.3g of Dye 1 pg-abs	Coloured polypren pg-abs	Dye-bath pg-abs	Outlet [a)] pg-abs
Σ TCDD	ND	ND	ND	ND
Σ PCDD	3	192	24	216
Σ H6CDD	247	2497	345	2842
Σ H7CDD	586	7765	869	8634
OCDD	1778	23812	2938	26750
Σ TCDF	210	320	24	343
Σ PCDF	128	343	57	400
Σ H6CDF	228	329	25	354
Σ H7CDF	543	57	10	67
OCDF	24	34	ND	34
Sum PCDD/F	4275	35414	4292	39706
Sum 2,3,7,8 PCDD/Fs	2291	27224	6634	33858

[a)] Sum of absolute amounts of PCDD/Fs in coloured polypren and in dye-bath

Conclusion

In two disperse black dyes, a mixture of anthraquinone disperse and azo-disperse dyes (Dye 1, Dye 2), considerable level of PCDD/Fs was determined, with the OCDD as the dominant homologue. Concentrations are below the restricted limits. In other dye samples analysed dioxins are present in trace amounts. We suggest replacing contaminated dyes by less toxic ones.

Distribution of dioxins and their fate during textile processes were investigated. After textile finishing processes the content of the PCDD/Fs was approximately tenfold higher. There is strong evidence that PCDD/Fs are formed from precursor compounds in contaminated dyes during textile finishing processes.

In our next work the chemistry of disperse dyes will be further investigated. Distribution of dioxins and their fate during textile processes will be investigated.

Emphasis will be laid on to photo transformation processes of dioxins in textile wastewaters and textiles, coloured with contaminated dyes. Use of ultraviolet light (UV) for degradation and elimination of organic pollutants in contaminated wastewaters is now a common process. Textile wastewaters are differentiated in quantities and types of suspended particles and in dissolved organic materials that could either retard or enhance the photolysis of PCDD/Fs. Irradiation of waste waters with powerful (up to 300 kW) UV lamps with catalysts as H_2O_2, NaOCl, Fenton's regent, etc. could be the source of lower chlorinated and more toxic dioxin congeners.

References

[1] Ballschmiter K., Bacher R.: *Dioxine*, VCH Verlagsgesellschaft, Weinheim, 1996.

[2] Stanmore B.R.: Comb. Flame **136**, 398.

[3] US-EPA.: Exposure and Human Health Reassessment of 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD) and Related Compounds-Part I: Estimating Exposure to Dioxin-Like Compounds-Volume 2: Sources of Dioxin-Like Compounds in the United States (Available from http://www.epa.gov/ncea/pdfs/dioxin/part1/volume2/chap10.pdf)

[4] Toolkit (2003): Standardized Toolkit for the Identification and Quantification of Dioxin and Furan Releases-1st Edition, May 2003. UNEP Chemicals, Geneva, Switzerland (Available from http://www.chem. unep.ch/pops/pdf/ toolkit/toolkit.pdf)

[5] Hagenmaier H.: Chemosphere **15**, 1421 (1986).

[6] Horstmann M.: Chemosphere 27, 113 (1993)

[7] Horstmann M., McLachlan M.S.: Chemosphere **31**, 2579 (1995).

[8] Horstman M.: Organohalogen Comp.**11**, 417 (1993).

[9] Williams D.T.: Chemosphere **24**, 169 (1992).

[10] Santl H.: Chemosphere **29**, 1995 (1994).